

## ● Introduction

### 1. What is a coordination compound?

Complex is a real chemical entity having its identity formed by a definite ratio of metal and ligand putting in a definite stereochemistry.

Double salt in a coordinating solvent is nothing but a complex salt.

## ● Retrospection

1. Simple salt
2. Double salt
3. Transition and nontransition elements → differences in reactivities
4. Coordination number, stereochemistry, isomerism
5. Ligands → different types
6. Ligational motifs
  - a) Halides → terminal/bridging, atomic/ionic bond
  - b) pseudohalides → ambidenticity, versatility, polyatomic rod
  - c) Aquo-hydroxo → protic equilibria
  - d) Oxo → polymetallic complexes
  - e) Carboxylates, polycarboxylate, Oxalate
  - f) Amines → synthon for Schiff-bases, football molecule
  - g) Amides → precise structural control
  - h) Polypyridines → photoactivity
  - i) Azoimines → isomeric products, chelate loops
  - j) Phosphines → trans-chelation
  - k) Carbonyls and nitrosyls → Organometallic compounds, clusters
  - l) Azophenols → colouring agents
  - m) Dioxolones → Oxidation state tautomerism
  - n) Schiff-bases → chelator, congregator, allosterism



## Questions

(16)

1. For qualitative detection of the individual ions you will get the number of radicals for Mohr-Salt is:  
a) 4      b) 2      c) 3      d) no detectable ions
2. Example of a non-innocent ligand is:  
a) NO      b) NO<sub>2</sub>      c) CN<sup>⊖</sup>      d) SCN<sup>⊖</sup>
3. Example of a non-classical ligand is:  
a) C<sub>2</sub>H<sub>4</sub>      b) NH<sub>3</sub>      c) OH<sup>-</sup>      d) CO
4.  $\pi$ -bonding stability in the coordinated ligand will prefer:  
a) Cis-complex      b) trans complex      c) equal mixture of both      d) no effect on geometry

## Further reading

1. Innocent and non-innocent ligand
2. Cis-chelator and trans chelator
3. Homoleptic and heteroleptic complex
4. Homogenous and heterogenous catalyst
5. Electron reservoir ligand (Hydroquinone — semiquinone — quinone)
6. Electron compound and electron sponge compound
7. HSAB-principle and borderline metal ion
8. Macrocyclic ligand and football molecule
9. Coordination number and hapticity
10. Quasi-aromaticity and Super-aromaticity

## Remember the chemical formulae (determine the oxdo. state of the metal ion)

1. Mohr-salt      2. Sodium nitropruside      3. Sodium-cobalt nitrite
4. Wilkinson catalyst      5. Cis-platin      6. Zeises salt      7. Millon's base
8. Vasca's complex      9. Brown-ring compound      10. Magnus green
11. Blue vitriol and green vitriol      12. Epsom salt      13. Molybdenum blue
14. Turnbull's blue      15. Belluci's salt      16. Prussian blue



## 7. Coordinate covalent bond

(2)

### Theories of coordinate bond

- The valence bond theory
- The valence shell electron pair repulsion theory
- The electrostatic theory
- The crystal field theory: The essence of this theory is that the five d-orbitals which are degenerate and equal in energy in the gaseous metal ion, become differentiated in the presence of the electrostatic field due to the ligands (the crystal field). It is the symmetry of this field, or its regular geometrical properties, which gives the theory its name. Though originally applied to crystalline solids, it is equally applicable to any orderly arrangement of electrically interacting particles such as a single complex. In particular, those orbitals lying in the direction of the ligands are raised in energy with respect to those lying away from the ligands. By preferentially filling the low-lying levels of the orbitals, the d-electrons stabilise the system, as compared to the random filling of the d-electrons. The gain in bonding energy by preferential filling of the levels is called as C.F.S.E. It is caused by the distribution of charge around the central atom of the complex not being symmetrical, as assumed in the earlier theories.

### 8. Properties of complex compounds affected by C.F.S.E

1. Stereochemistry
2. Redox potentials
3. Stability of the complexes
4. The coordinate bond energy
5. The effective ionic charge

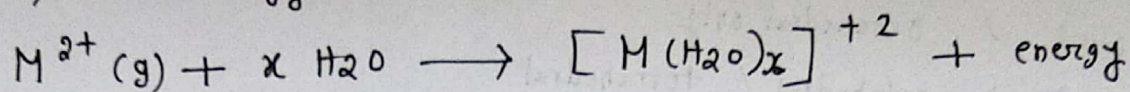
Modern theory of coordinate linkage  $\rightarrow$  Ligand field theory



## 9. Properties of coordination compounds affecting reaction mechanism (3)

### a) Thermodynamic properties :

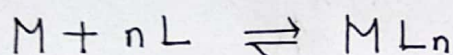
#### i) Hydration energy



#### ii) Lattice energy



#### (iii) Stability constant



[★ Retrospection: (1) Stepwise and overall formation constant and relation between them

(2) Stability and instability constants

(3) Free energy, reaction profile, exothermic and endothermic reaction

(4) Lattice energy, solvation energy

(5) Variation of ionic radii, lattice energy, hydration energy

[See R.L. Dutta]

(6) Factors affecting stability of the metal complex:

a) The nature of metal ion  $\rightarrow$  size, charge, CFSE (Irving-William series), polarisability, electronegativity

b) Nature of the ligand  $\rightarrow$  basicity, nucleophilicity, polarisability, chelate effect,  $\pi$ -bonding, macrocyclic effect

c) Nature of solvent ]

### <b> Kinetic properties :

Points : i) Lability and inertness of a complex system

ii) Difference between stable and inert system as well as unstable and labile system

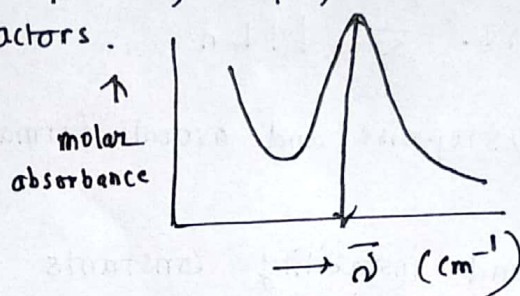
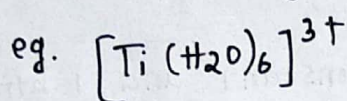


### (c) Stereochemical property

- Co (II)  $\rightarrow$  Octahedral / Tetrahedral  
Ni (II)  $\rightarrow$  Octahedral / square planar / rarely tetrahedral  
Cr (III)  $\rightarrow$  Octahedral only  
Fe (III)  $\rightarrow$  Octahedral / tetrahedral  
Cu (II)  $\rightarrow$  Distorted octahedral (arises due to uneven population and uneven relation)

(d) Magnetic properties  $\rightarrow$  described by electrostatic crystal field theory

(e) Spectral property  $\rightarrow$  position, shape, sharpness, width of bands are important guiding factors.



### Factors affecting the rate of reaction

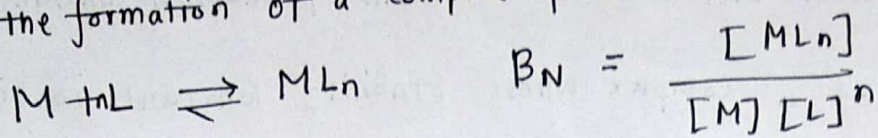
1. Order of reactions
2. The effect of 'd' electron structure of the metal ion
3. Steric effect on the substrate and on the intermediate
4. Influence of concentration and nature of the incoming ligand
5. The effect of net charge on the complex ion
6. The linear free energy relationship
7. The influence of  $\pi$ -bonding
8. Influence of temperature and external pressure
9. Effect of pH of the medium and the nature of solvent
10. Effect of ion-exchange
11. Hammett Relationship



## Stability and lability of complexes:

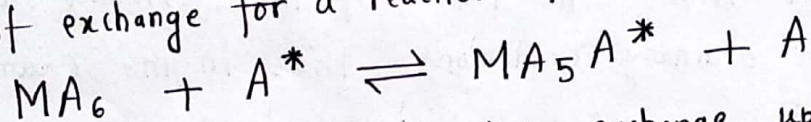
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The stability of complex  $ML_n$  in the thermodynamic sense is expressed in terms of a formation constant, which is the equilibrium constant for the formation of a complex from the constituents in solution.



The higher the value of  $B_N$ , the greater the stability of the complex. The thermodynamic stability of the complex, however, is not the only factor influencing the observed behaviour of a complex, the rate of reaction of a complex also plays a vital role. The term 'labile' is applied to very reactive complexes, whereas, less reactive complexes are called 'inert'. There is, of course, no sharp division between these two classes, but rather, there exists a continuous gradation. H. Taube has defined 'labile' to mean systems where reactions are complete within the time of mixing (1 minute, room temperature, about 0.1M soln.).

The term 'inert' is used for reactants that are either too slow enough to follow at ordinary conditions by conventional technique. The most direct and least ambiguous test of lability is to measure the rate of exchange for a reaction of the type:



A labile complex will undergo immediate exchange upon mixing with tagged  $A^*$ . The term 'inert' must not be confused with the term 'stable'. One has kinetic aspect, the other has thermodynamic sense. A thermodynamically stable complex always does not need to be inert.

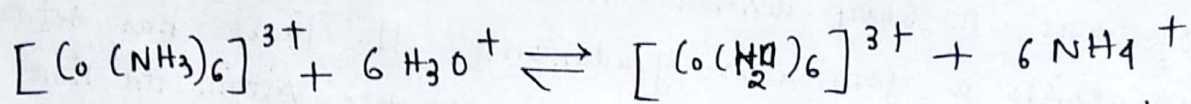
The following complexes illustrates the lack of correlation between stability and inertness.

<u>Complex</u>	<u>Stability const. (<math>B_N</math>)</u>	<u>exchange rate</u>
$[Ni(CN)_4]^{2-}$	$10^{30}$	Very fast
$[Hg(CN)_4]^{2-}$	$10^{42}$	Very fast



1. What do you mean by Stability and lability of a complex?
2. Derive the relation between stepwise and overall formation constant.
3. Give one example of a complex whose stability constant is high but labile in nature.
4. Discuss: Stability and inertness do not go parallel always

● The complex ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is very unstable (thermodynamically) in acid medium, having a considerable tendency to dissociate.



For the above reaction, the eqm. const. is very high, in the order of  $10^{25}$ . But actually, the ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  persists unchanged for weeks in acidic solution. In fact, the complex  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  can be crystallised from hot, aqueous HCl without any considerable decomposition. This is due to the fact that, the rate of the forward reaction is extremely slow under ordinary conditions. Thus in the example cited,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is unstable but inert in the aqueous acid.

● Similarly some other complexes may be stable as well as inert  $\rightarrow$  eg.  $[\text{Fe}(\text{CN})_6]^{4-}$   
or, unstable and labile as well.

Thus, ① stability and inertness are not parallel.

② unstability and lability are not parallel.

③  $K_{\text{eqm}}$  and  $K_r$  do not correspond parallelly always.

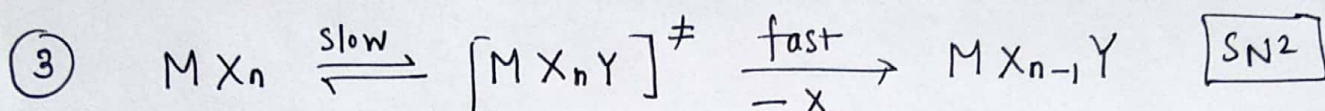
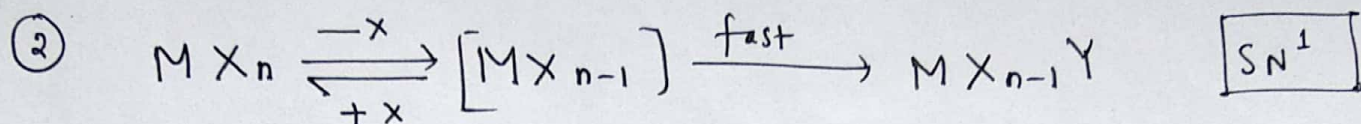
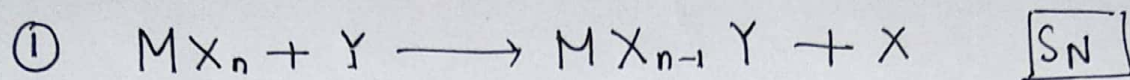
④  $\Delta G^\circ$  when  $-ve$ , does not always mean low activation energy



# Application of Crystal field theory in predicting lability of complexes: (5)

## Ligand Substitution reactions

### Nucleophilic Substitution reactions

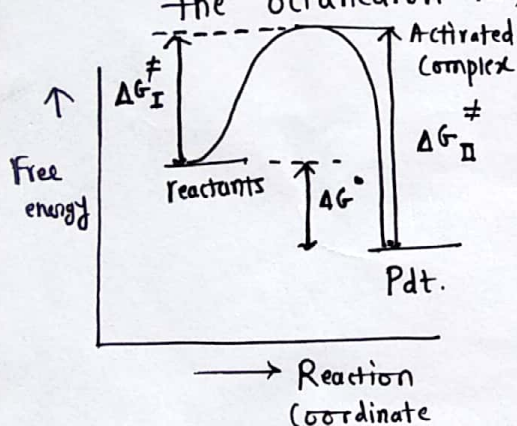


$$[(C.F.S.E.)_{oct} - (C.F.S.E.)_{intermediate}] = \Delta E_a$$

$\Delta E_a$  = Crystal field activation energy

$\Delta E_a$  should be zero or negative positive. If it is -ve, then

the octahedron may be unstable, or may be distorted in nature.



$\Delta G^\ddagger_I$  = Free energy of activation for forward reaction

$\Delta G^\ddagger_{II}$  = " " " " " backward "

$\Delta G^\circ$  = Free energy of reaction

$$K_r = \frac{KT}{h} e^{-\Delta G^\ddagger/RT}$$

Crystal field theory has been applied with moderate success to the problem of relative reactivity of Octahedral complexes. In order to explain the kinetic features of reactions of complexes on the basis of crystal field theory, it is necessary to calculate the C.F.S.E of various 'd' electrons-configuration in both weak field and strong field for a regular octahedral structure and intermediate expected to be formed in the transition state for the two plausible mechanism  $SN^1$  and  $SN^2$ :

- a) square pyramidal      b) Pentagonalbipyramidal

The difference between C.F.S.E. of octahedral structure and CFSE of the intermediate (sq. py / pbp) is considered to be its contribution towards



(6)

System	Strong field cases		Weak field cases	
	$S_N^1$	$S_N^2$	$S_N^1$	$S_N^2$
$d^0, d^1, d^2, d^{10}$	0	0	0	0
$d^3 \longrightarrow$	2.00	4.26	2.00	4.26
$d^4 \longrightarrow$	1.43	2.98	0	1.07
$d^5 \longrightarrow$	0.86	1.70	0	0
$d^6 \longrightarrow$	4.00	8.52	0	0
$d^7 \longrightarrow$	0	5.34	0	0
$d^8 \longrightarrow$	2.00	4.26	2.00	4.26
$d^9 \longrightarrow$	0	1.07	0	1.07

$S_N^1$  path (Square pyramidal intermediate)

→ reactivity decreases

$S_N2$  pathway (pentagonal bipyramidal intermediate)

2. Weak-field cases  $\underbrace{d^0, d^1, d^2, d^5, d^6, d^7, d^{10}}_{\text{labile}} \gg \underbrace{d^4, d^9}_{\text{inert}} > d^3, d^8$

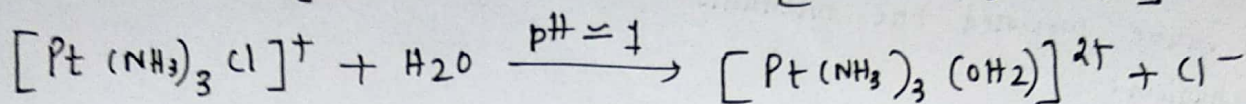
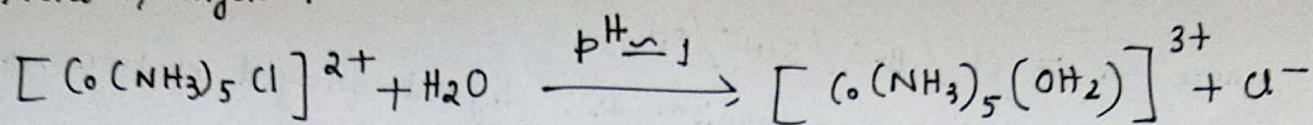


# Types of inorganic reactions

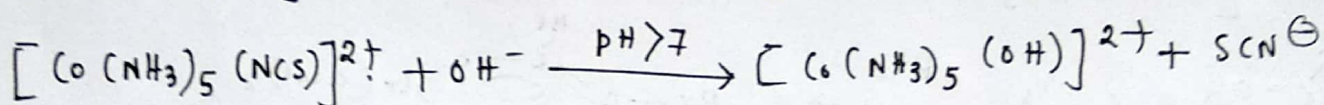
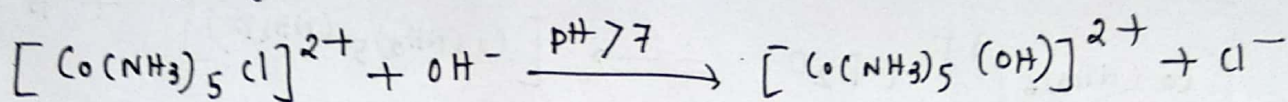
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## 1. Substitution reaction

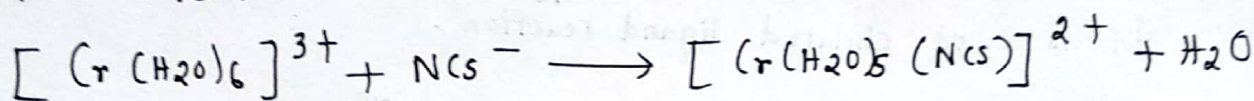
a) Acid hydrolysis :



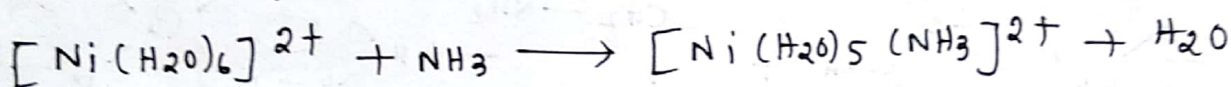
b) Base hydrolysis :



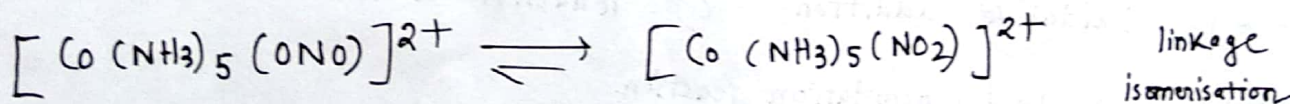
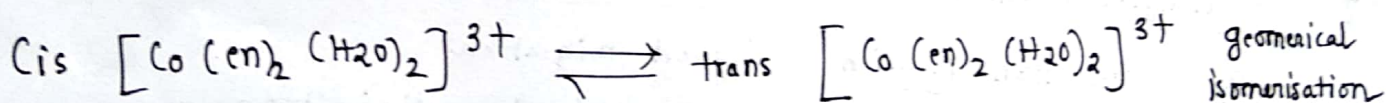
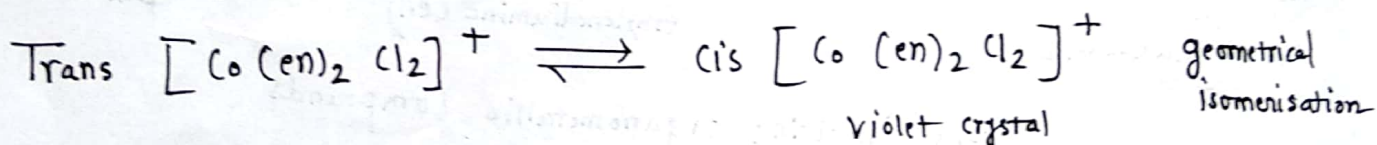
c) Anation reaction :



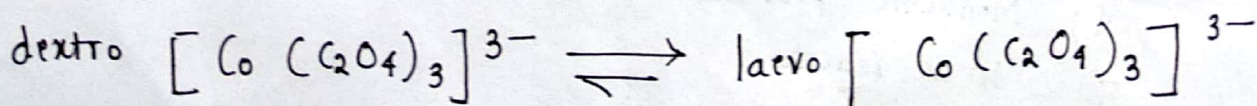
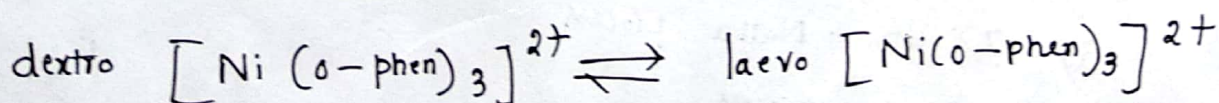
It is deaquation reaction.



## 2. Isomerisation reaction

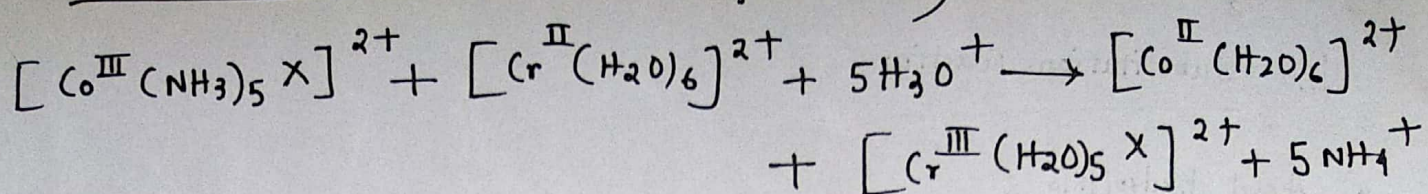


## 3. Racemisation reaction





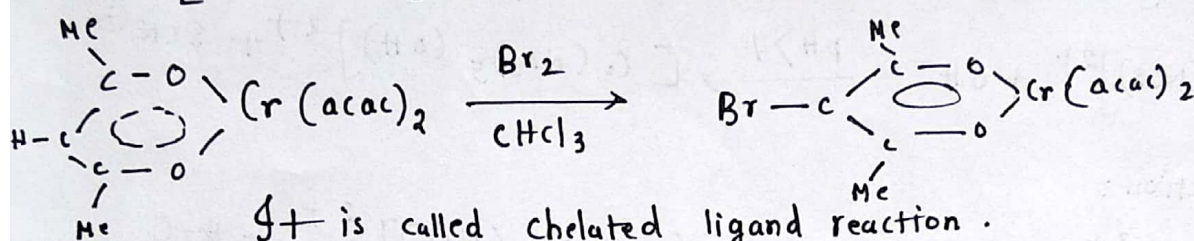
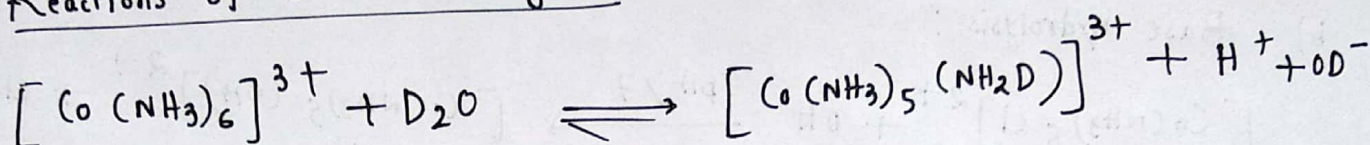
④ Oxidation-reduction (electron transfer reaction)



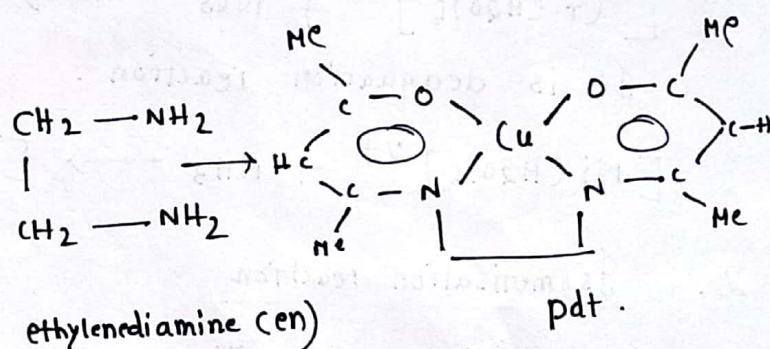
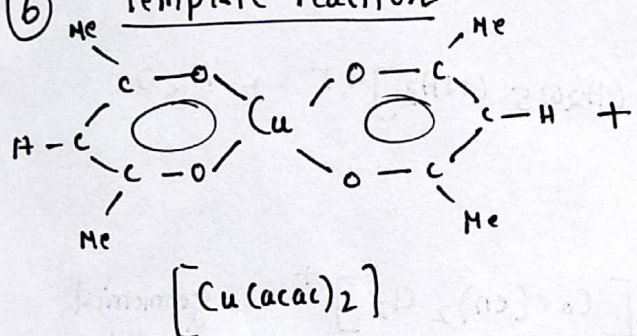
Where  $X^- = Cl^- / Br^- / SCN^- / OH^-$

H. Taube proposed the mechanism as: ligand-bridged electron transfer mechanism.

⑤ Reactions of coordinated ligands



⑥ Template reaction



⑦ Catalytic reactions involving organometallic compounds

- Insertion reaction / ligand migration
- Oxidative addition
- Reductive elimination

Examples:

- Hydroformylation reaction
- Wilkinson catalyst (Hydrogenation reaction)
- Zeigler - Natta process
- Monsanto process
- Heck reaction
- Water gas shift reaction
- Hydrocyanation, hydrosilation, olefin metathesis



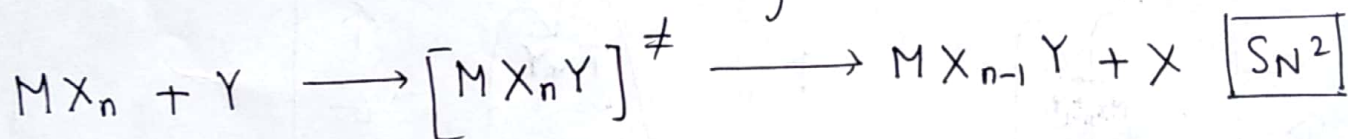
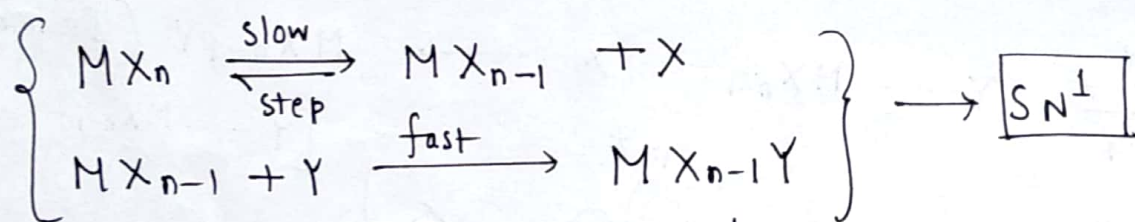
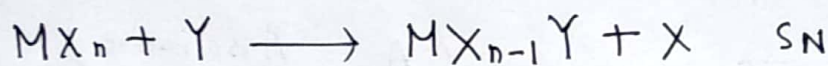
# Inorganic reaction mechanism

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Mechanism: By mechanism it means all the individual elementary processes involving molecules (atoms, ions, radicals included) that take place simultaneously or consecutively producing the observed overall reaction. It is also understood that, the mechanism of a reaction should give a detailed stereochemical picture of each step as it occurs. This implies a knowledge of the so called activated complex and transition state not only, but also in terms of geometry such as intermediate bond distances and angles.

## ● Substitution reactions

Classifications of mechanism:



Terminology regarding associative (A), dissociative (D) and interchange (I) process:

- A [ (iii)  $S_N^2$  (lim.)  $\rightarrow$  Here r.d.s. involves only bond making and there is definite evidence of increased coordination no. in the intermediate.
- D [ (i)  $S_N^1$  (lim)  $\rightarrow$  Here bond breaking is important in a r.d.s. as there is definite evidence of reduced coordination no. in the intermediate.
- (ii)  $S_N^1$ : Here, there is no such definite evidence of reduced c.N. but otherwise, satisfies the requirement of dissociative mechanism.

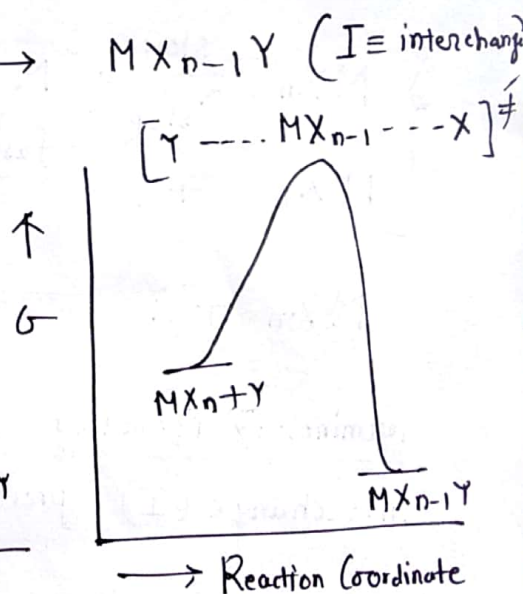
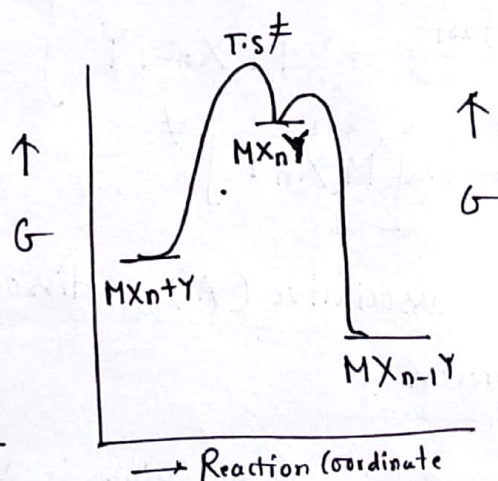
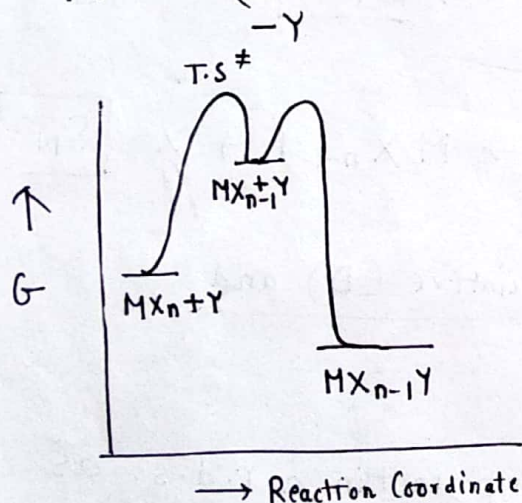
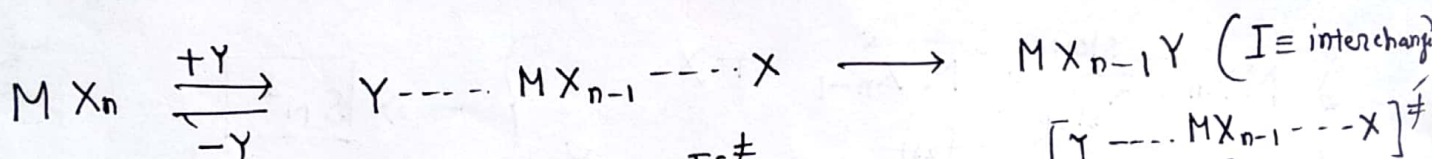
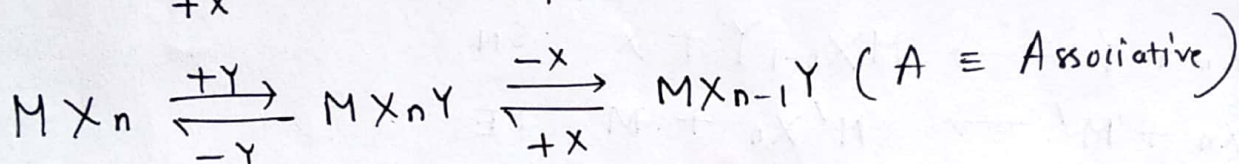
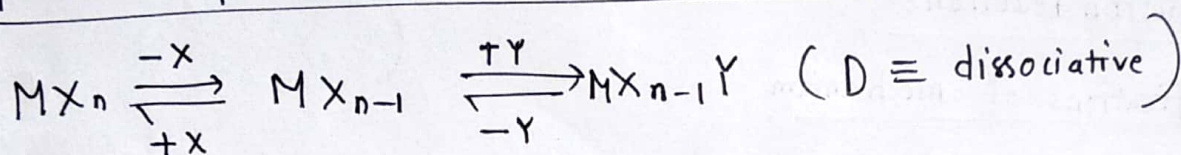


D  $\left[ \text{SN}^2 \rightarrow \text{Here r.d.s. involves about equal participation of bond making and bond breaking process. There is no such evidence of increased e.N. in the intermediate.} \right]$  (10)

Terminology proposed by C.H. Langford and H.B. Grey

- ① Stoichiometric mechanism  $\rightarrow$  This indicates the sequence of elementary steps by which the overall reaction takes place.
- ② Intimate mechanism  $\rightarrow$  This indicates the details of the activation process and the energetics for coordination of an activated complex.

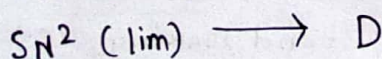
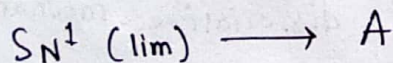
pictorial representation for A, D, I processes



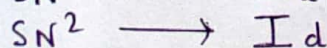
dissociative process (D)

Associative process (A)

### ● Compound terminology



$\text{I}_a$  and  $\text{I}_d$  are in between.





1. Define dissociative, associative and interchange process.
2. Draw energy profile for A, D, I processes.
3. Among A, I, D mechanisms, which one is a concerted process?
4. The octahedral and ~~tetrahedral~~ sq. planar complexes of  $M(III)$  or  $M(II)$  when goes substitution, the geometry of the intermediates are different for each cases. What are those?

MCQ type

1. In the intermediate of a substitution reaction, the coordination number for a 3-d metal ion has appeared to be 7. The process is  
a) Associative b) dissociative c) interchange d) cannot be told.
2. Intermediate for the interchange process:  
a) easy to isolate b) difficult to isolate c) isolation depends on stability of the intermediate d) b is true because there is no distinct intermediate
3. Oxidative addition and reductive elimination are the steps of:  
a) Isomerisation b) Substitution c) Catalytic reaction d) Racemization
4. Hydrolysis of  $[Co(NH_3)_5Cl]^{2+}$  at pH 5 will lead to:  
a)  $[Co(NH_3)_5(OH_2)]^{3+}$  b)  $[Co(NH_3)_5(OH)]^{2+}$  c) both a+b  
d)  $[Co(H_2O)_6]^{3+}$
5. You can determine the stoichiometry of the inner-sphere ligands of the substrate  

$$\left\{ \begin{array}{l} [Co^{III}(NH_3)_x(S_2O_3)_y] + OH^- \longrightarrow [Co^{III}(NH_3)_x(OH)_y] + S_2O_3^{2-} \\ \text{with reaction with } OH^- \text{ with it by :} \end{array} \right.$$
  
a) iodometry b) iodimetry c) Acid-base titration d) Can't be determined by the reaction



6. If  $\Delta G^\ddagger$  is strongly influenced by incoming group bond formation then the mechanism is supposed to be: (12)

- a) associative    b) dissociative    c) interchange    d) may be a or c

7. If the rate of substitution reaction for a constant nucleophile varies strongly with the nature of the most labile ligand present in the complex, then the mechanism is supposed to be:

- a) associative    b) dissociative    c) interchange    d) cannot be told

8. Reaction of  $[PtCl_4]^{2-}$  and  $OH^-$  if proceeds via substitution pathway, we can ascertain it by:

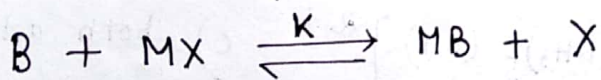
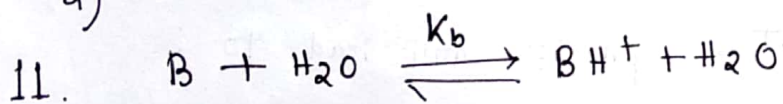
- a) conductance measurement    b) precipitation titration    c) Spectrophotometry  
d) all of the above.

9. Racemisation reactions of the complex compounds can be studied by:

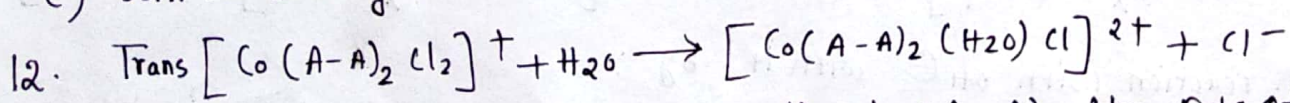
- a) I.R. spectroscopy    b) Polarimetric method    c) determining the pH  
d) by UV-visible spectroscopy

10.  $[Co(NH_3)_5Cl]^{2+}$  reacts 100 times ~~faster~~ slower than  $[Co(NH_3)_5Cl_2]^+$  with water. It suggests:

- a) Associative mechanism    b) dissociative mechanism    c) interchange process  
d) Can't be told.



- a)  $K_b$  represents basicity of B and K represents nucleophilicity.  
b)  $K_b$  " nucleophilicity of B and K " basicity  
c) both represent basicity    d) both represent nucleophilicity  
e) both are actually same because nucleophilicity towards  $H^+$  is termed as basicity.



With increasing bulk of the bidentate ligand (A-A), the rate of the substitution reaction:

- a) Increases    b) decreases    c) independent of the bulk    d) cannot be told unambiguously

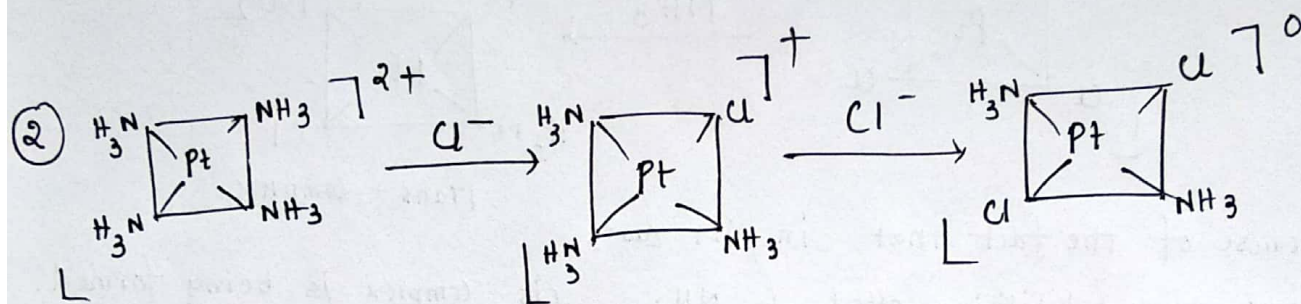
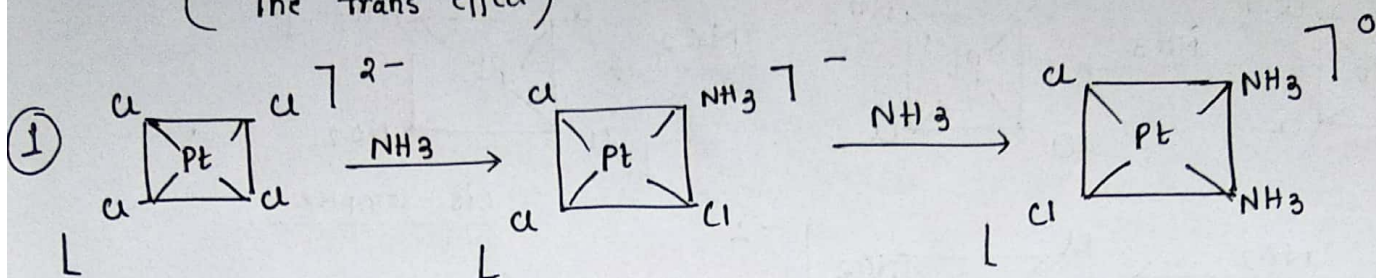


# Substitution reaction in square-planar complexes

13

Reactions of square planar platinum (II) complex :

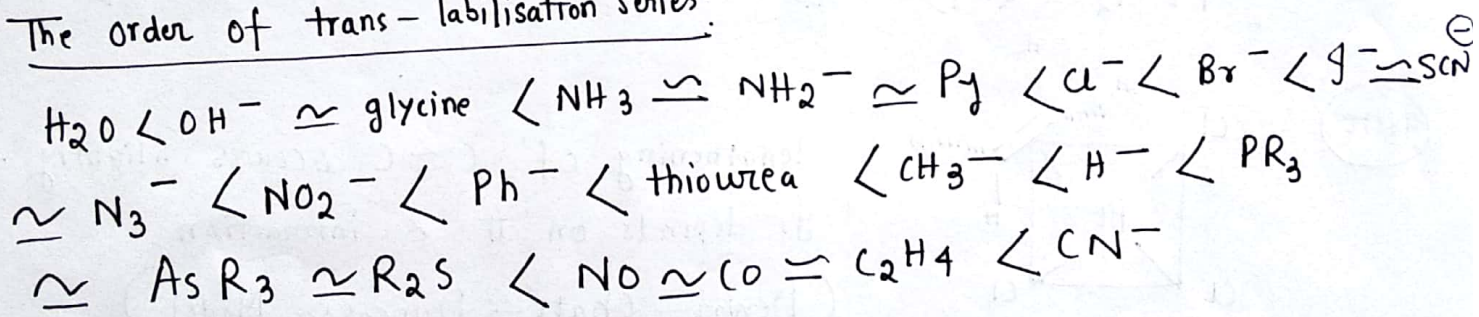
(The trans effect)



Trans effect series : (based on qualitative and semiquantitative observations)

The ligands commonly found in Pt(II) complexes have been arranged into an approximate increasing order of their trans-directing influence, known as the trans-effect series, which is as follows:

The order of trans-labilisation series:



$\text{H}_2\text{O}$  to  $\text{Py}$   $\rightarrow$  Weak trans effect

$\text{Cl}^-$  to  $\text{N}_3^-$   $\rightarrow$  Moderate effect

$\text{NO}_2^-$  to  $\text{H}^-$   $\rightarrow$  large effect

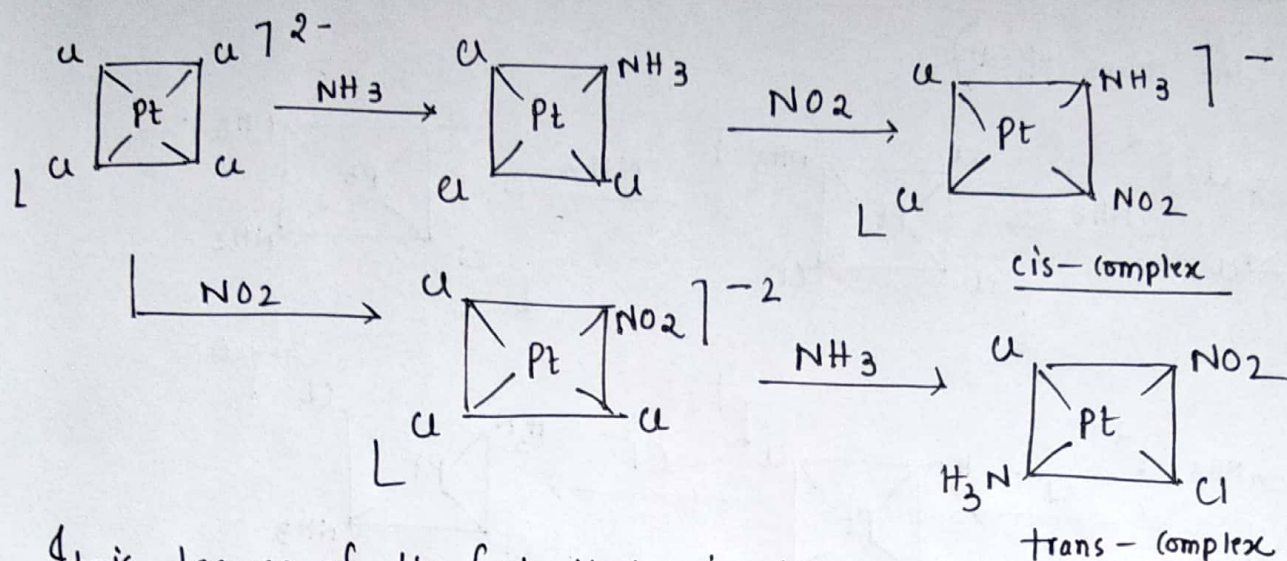
$\text{PR}_3$  to  $\text{CN}^-$   $\rightarrow$  Very large effect



# Synthesis of isomeric Pt (II) complexes

14

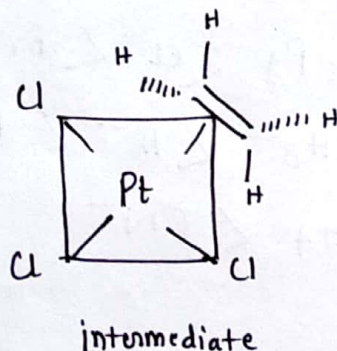
a) cis and trans  $[Pt(NH_3)(NO_2)Cl_2]^-$  complex



It is because of the fact that in 1st case, due to weak trans-labilising effect of  $NH_3$ , cis-complex is being formed. For the 2nd case, stronger trans-effect of  $-NO_2$  gr. leads to trans labilisation of  $Cl^-$  to form trans complex.

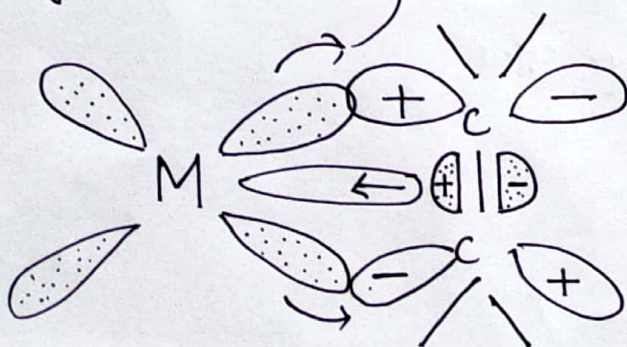
Task: Design pathway of synthesis of cis and trans  $[PtCl_2(C_2H_4)(NH_3)]^0$  from tetrachloroplatinate (II) complex.

Note



lengthening of  $C=C$  occurs slightly. It depends on  $\pi-\delta$  interaction (Dewar-Chatt-Duncanson Model)

Remember  $\rightarrow$  Structure of Zeises salt (first synthesised organometallic salt)



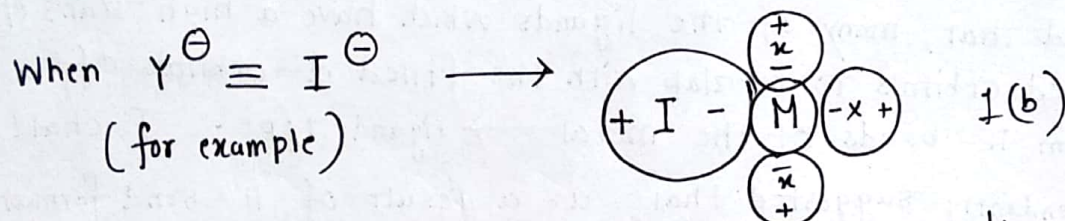
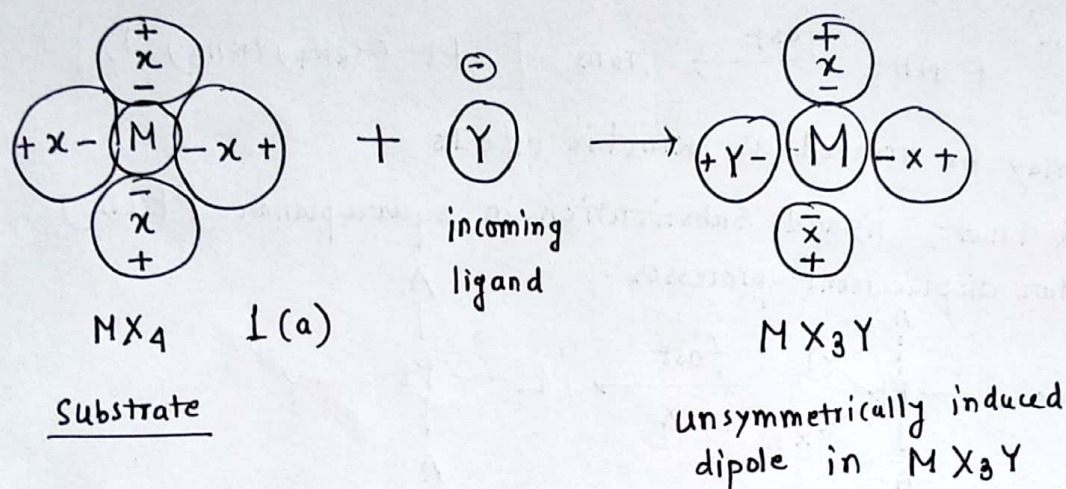


Thermodynamic effect and Kinetic effect :

The Source of the trans effect can be classified into thermodynamic and Kinetic factors. The thermodynamic factor refers to Weakening of the bond to the leaving gr. of the reactant (Called trans-influence)

Kinetic factor refers to the Stabilisation of transition state by the trans ligand.

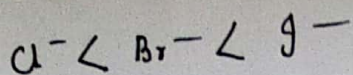
A] The polarisation theory (Proposed by Grinberg) → Thermodynamic effect



Mutual polarisability of the central ion and the ligands result in induced dipoles in both. If the four ligands in the complex are identical (as in the substrate) then there is symmetrical distribution of the induced dipoles and the resultant dipole in the central ion is zero. [fig. 1a]. If one ligand differs from the other three, there is no longer a mutual compensation in the induced dipole and there will be a resultant dipole on the central atom and on the overall structure as a whole. [fig. 1b]. On the basis of such a picture, the suggestion is made that, if Y is more polarisable than X, the central atom is intern, polarised in a way, such that, it is less positive directly opposite (trans) to Y, thereby weakening M-X bond trans to Y.

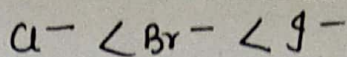


## Trans effect series



← goes parallel →

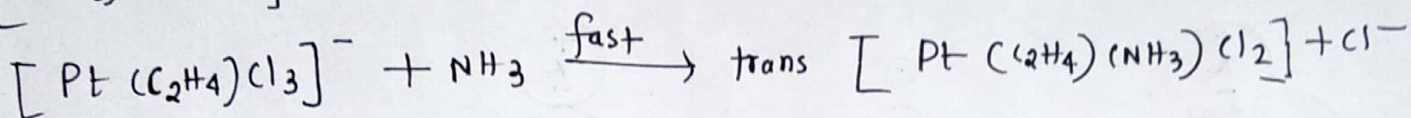
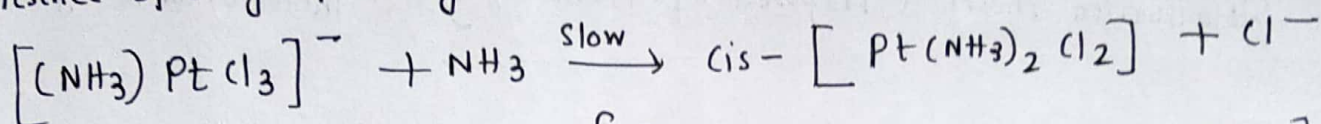
## Order of polarisability



(16)

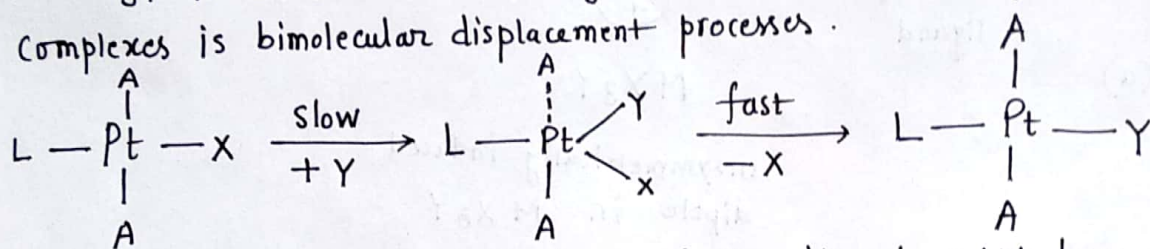
## [B] The $\pi$ -bonding theory: → kinetic effect

It is observed, that the rate of substitution in the presence of a strongly trans directing group is very much faster than the corresponding reaction in the presence of a group having a low trans effect.

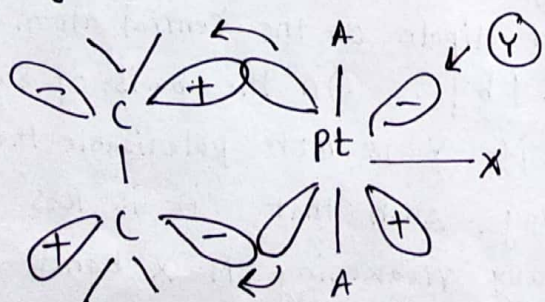


So, these effects may be treated as kinetic effects.

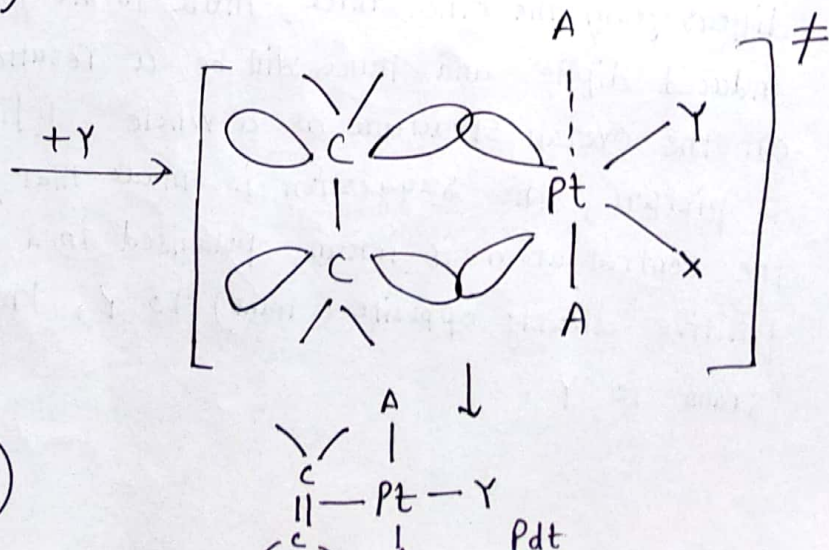
It is assumed that, ligand substitution in square planar  $Pt(II)$  complexes is bimolecular displacement processes.



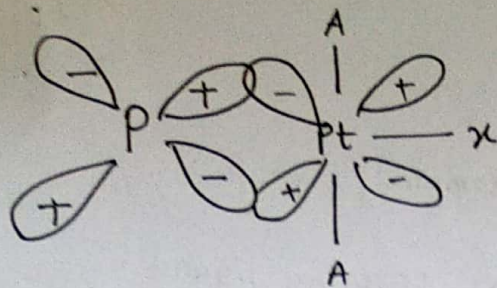
It has been observed that, many of the ligands which have a high trans effect have suitable unfilled orbitals to overlap with the filled d-orbitals of platinum (II) to form  $\pi$ -bonds of the metal → ligand type. J. Chatt and Orgel independently suggested that, as a result of  $\pi$ -bond formation of this type, there is a considerable reduction in the electron density in the filled  $d_{xz}$  orbital of  $Pt(II)$  in the vicinity of  $X$ , thereby facilitating nucleophilic attack by the incoming ligand in this region (region of least electron density).



$\pi$ -d  $\pi$  interaction  
(in case of  $C_2H_4$  ligand)







$d\pi-d\pi$  interaction  
(in case of  $PR_3$  type ligand)

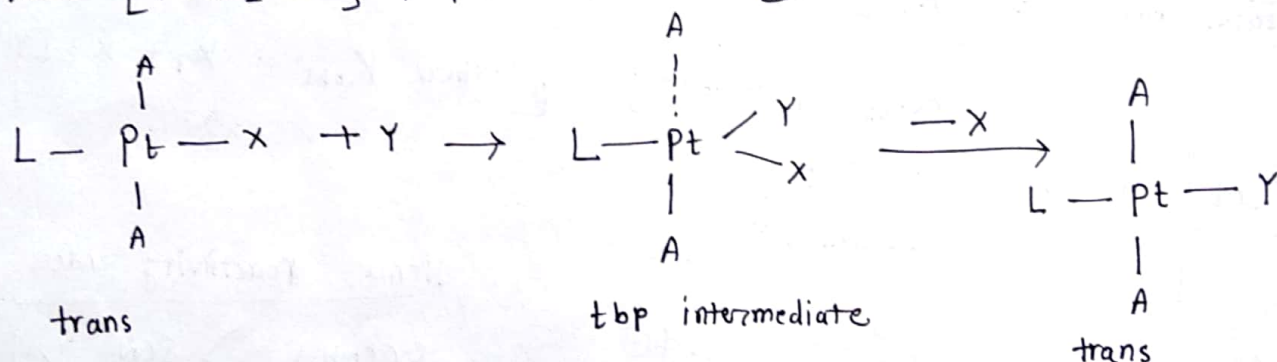
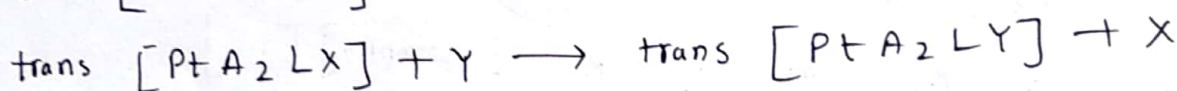
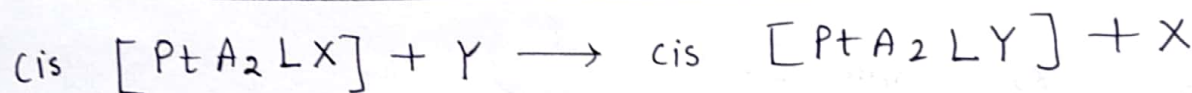
$\pi$ -bond formation. Therefore, the greater the  $\pi$ -bonding tendency of L, the greater the trans effect, because of its increased stabilising influence on the five coordinated intermediate.

On the basis of  $\pi$ -bonding (17) theory, the increased rate of trans-substitution has been explained as due to lowering of activation energy for the formation of the transition state. The lowering of activation energy results from the fact that the trigonal bipyramidal configuration in the transition state is more stabilised by

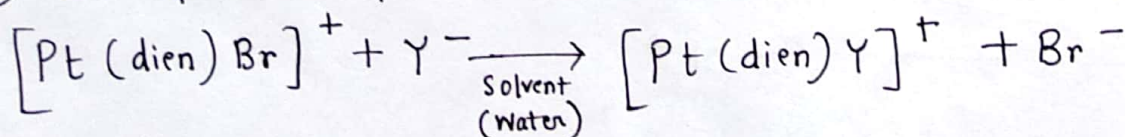
### ● Mechanism of ligand substitution in square planar $Pt(II)$ complexes:

Substitution in square planar  $Pt(II)$  complexes are bimolecular displacement process is supported by different kinds of experimental evidences.

#### ① Substitution occurs with steric retention



#### ② The dependence of rate of the reaction on the entering ligand:



dien = diethylenetriamine  $H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$

$Y^- = OH^-, Cl^-, I^-, SCN^-, SC(NH_2)_2$



Rate law :  $\text{Rate} = - \frac{d [\text{complex}]}{dt}$

(18)

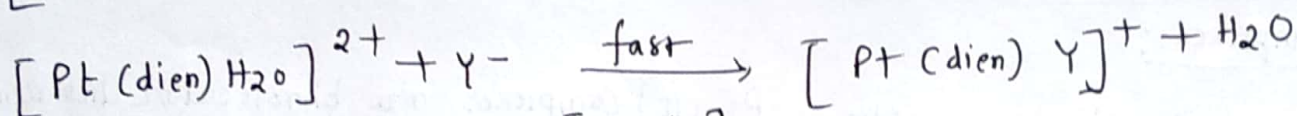
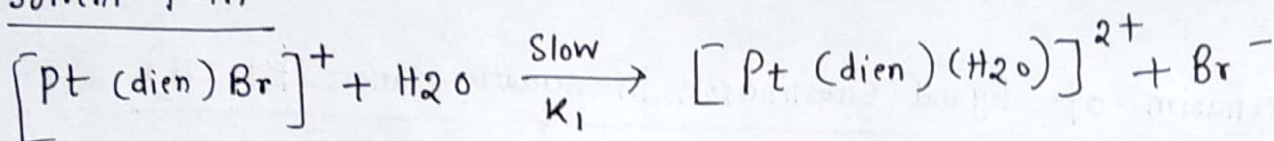
$$= k_1 [\text{complex}] + k_2 [\text{complex}] [Y^-]$$

③ The dependence of rate of the reaction on the entering ligand



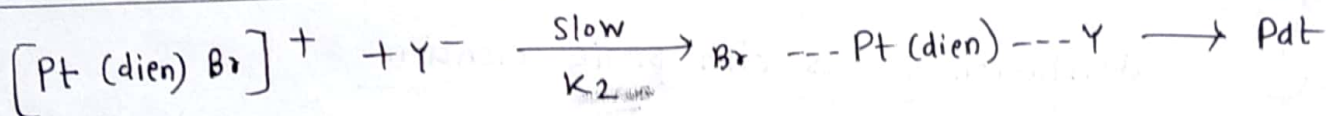
$$\text{Rate} = - \frac{d [\text{complex}]}{dt} = k_1 [\text{complex}] + k_2 [\text{complex}] [Y^-]$$

Solvent path



$$\therefore \text{Rate} = k_1 [\text{complex}]$$

direct displacement of ligands by incoming nucleophile

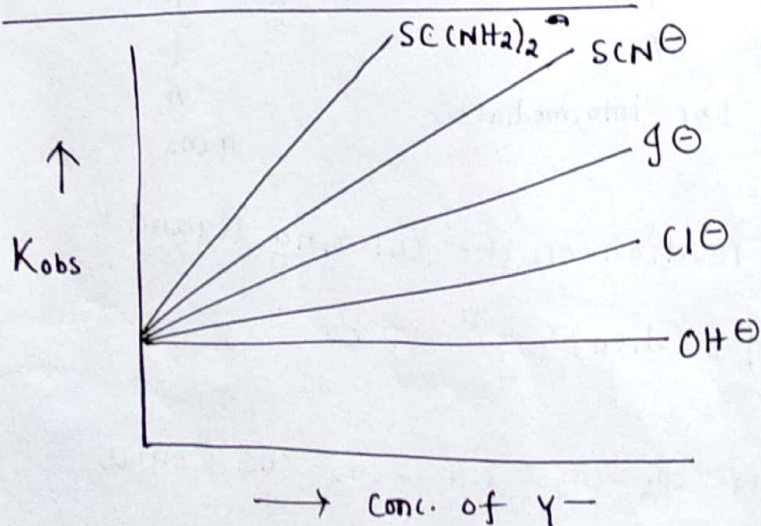


$$\text{Rate} = k_2 [\text{complex}] [Y^-]$$

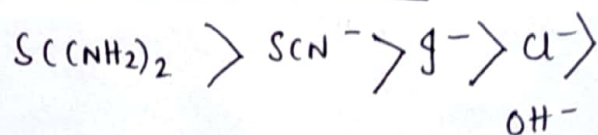
$$\text{Total rate} = k_1 [\text{complex}] + k_2 [\text{complex}] [Y^-]$$

$$= K_{obs} [\text{complex}] \quad [\text{where } K_{obs} = k_1 + k_2 [Y^-]]$$

● Plot of  $K_{obs}$  vs  $[Y^-]$



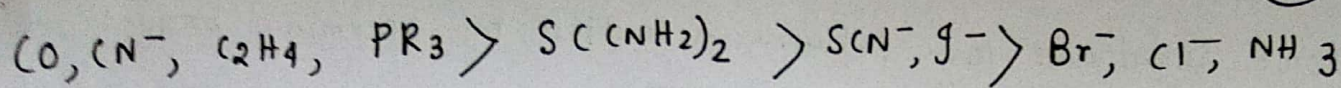
Hence, reactivity order





## Relative reactivity of different entering group

(19)



## Interpretation of the rate data

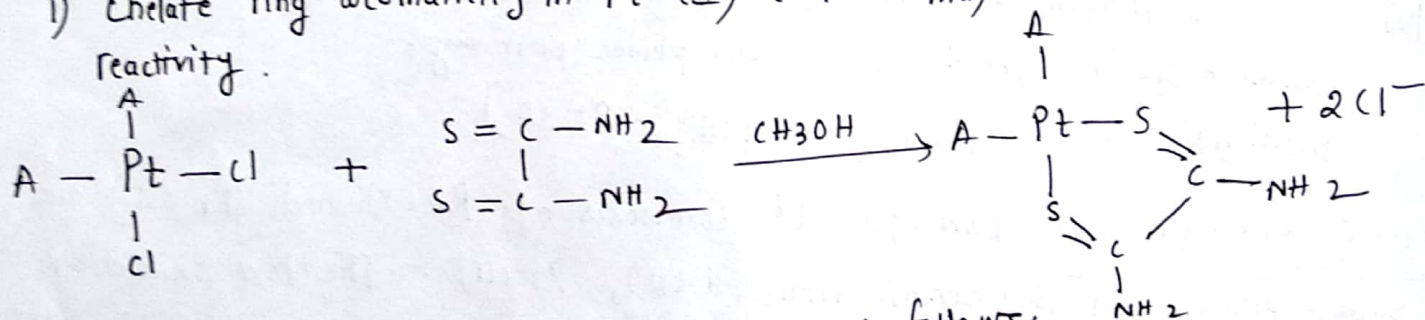
The average ligand reactivity order bears a remarkable resemblance to the trans effect order. Thus, a good trans labiliser is also a good entering group in the square planar substitution. It is expected for an associative (A) mechanism via a t<sub>5</sub>p geometry viz. increased coordination number in the intermediate.

## Effect of charge on the complex

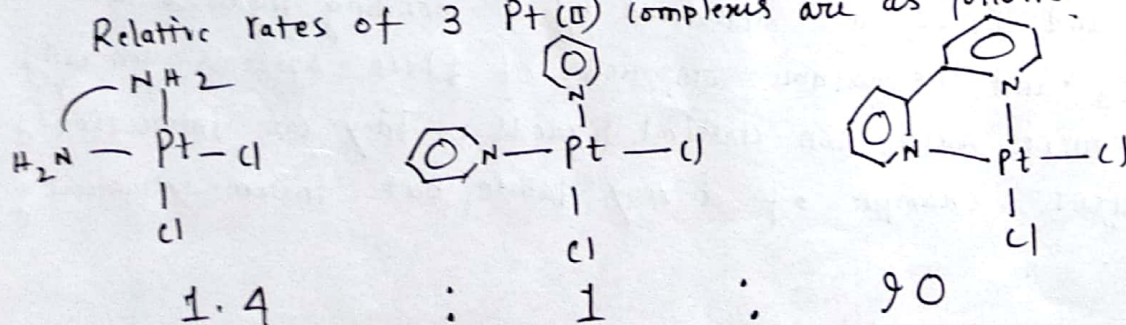
The effect of charge on the complex is one of the most conclusive evidence for an associative solvent path of the substitution reactions, in Pt(II) complexes in aq. soln. It appears from the rate data, that, there is lack of large rate effect in the aquation series of various Pt(II) complexes having different overall charges on the complexes. If the aquation reactions proceed through dissociative pathway, then separation of charges will lead to rate difference.

## Other factors

1) Chelate ring aromaticity in Pt(II) complexes may enhance their reactivity.



Relative rates of 3 Pt(II) complexes are as follows:





## (2) Neighbouring group participation (anchimeric assistance)

(20)

Some substituents may influence a reaction by becoming bonded or partially bonded to the reaction centre.

### Other square-planar systems undergoing substitution reactions

Gold (III), Pd (II), Low-spin Ni (II), Low spin  $d^8$  Rh (I),  
Low spin  $d^8$  Ir (I)

also  $d^9$  tetragonal Cu (II)  $\rightarrow$  shows similarities with square planar mechanism.

Gold (III): Iso-electronic with Pt (II) and shows some similarities as well as contrast with Pt (II). Complexes of Au (III) react approximately  $10^4$  times faster than those of Pt (II). The solvent path is much less important for reactions of Au (III) than for Pt (II). The nucleophilic properties of different reagents towards the Au (III) substrate parallel those for Pt (II).

Pd (II): These reactions are typical of square planar substitutions. The Pd (II) complexes are  $10^5$  times more reactive. This is in accord with a much weaker Pd-X bond strength. But there, solvent path makes an appreciable contribution to the overall rate of the reaction.

Solvent path contribution order  $\rightarrow$  Pd (II)  $>$  Pt (II)  $>$  Au (III)

Ni (II): Low spin  $d^8$  system forms square-planar geometry. Reaction mechanism is a typical of square planar pathway.

Reactivity order: Ni (II)  $>$  Pd (II)  $>$  Pt (II)

Rh (I) and Ir (I): Low spin  $d^8$  complexes of Rh (I) and Ir (I) are square planar and isoelectronic with Pd (II), Pt (II). The low oxidation states of Rh (I) and Ir (I) are stabilised by  $\pi$ -bonding ligands such as CO and  $PR_3$  and the stable compounds of these systems generally contain one or more such non-classical ligands. They can interestingly form an excellent example of a very labile but thermodynamically stable system.



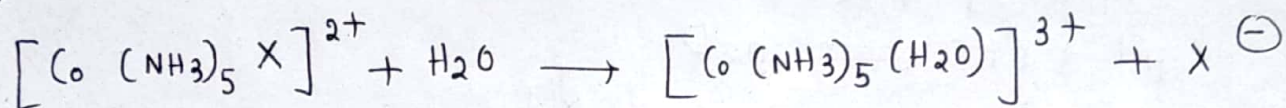
# Substitution reactions in octahedral complexes

## Order of reaction and reaction mechanism

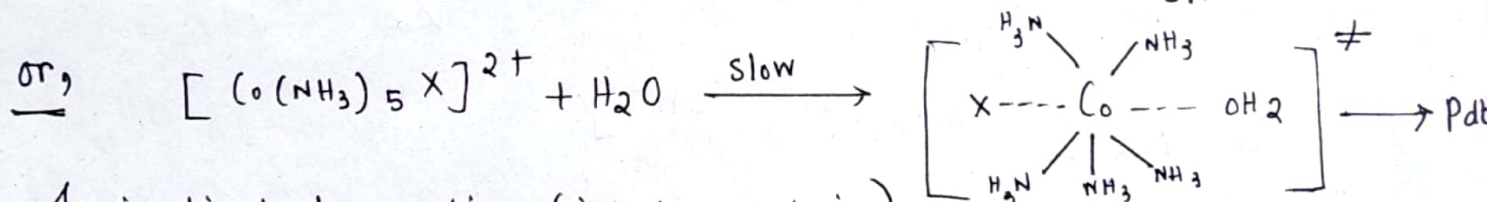
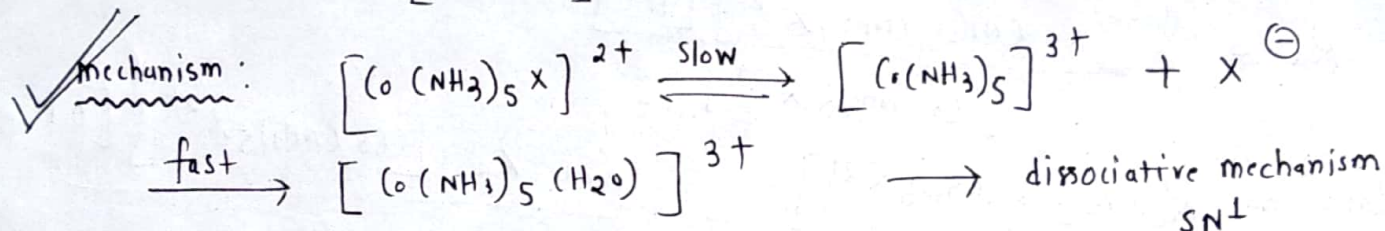
The fact that a system exhibits first or second order behaviour does not necessarily mean that an unambiguous reaction mechanism can thereby postulated. It is not correct to assume that a bimolecular reaction will show 2nd order rate law and vice-versa. This is due to the fact that, order and molecularity do not go parallelly.

## Types of kinetics followed by octahedral geometry

### 1) Acid-catalysed hydrolysis



$$\text{Rate} = k [\text{Substrate}]$$



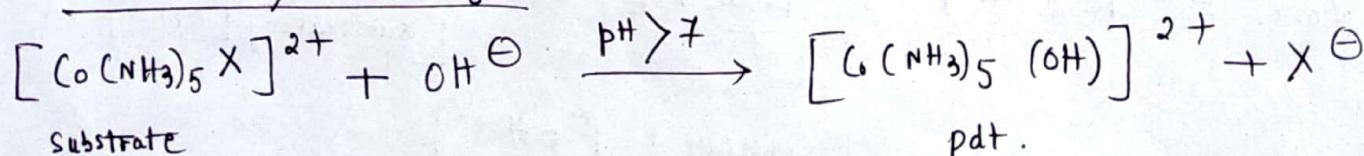
It is bimolecular reaction. (interchange mechanism)

$$\text{Rate} = k [\text{Substrate}] [\text{H}_2\text{O}]$$

Now,  $[\text{H}_2\text{O}]$  is almost constant.

Hence,  $\text{Rate} = k [\text{Substrate}]$  [where  $k$  = pseudo 1st order rate const.]

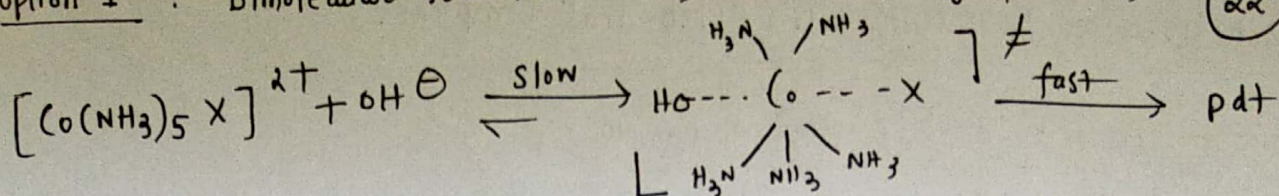
### 2) Base-catalysed hydrolysis



Rate law:  $-\frac{d[\text{Substrate}]}{dt} = k_2 [\text{Substrate}] [\text{OH}^-]$

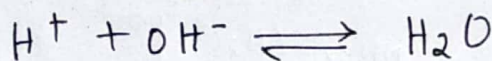
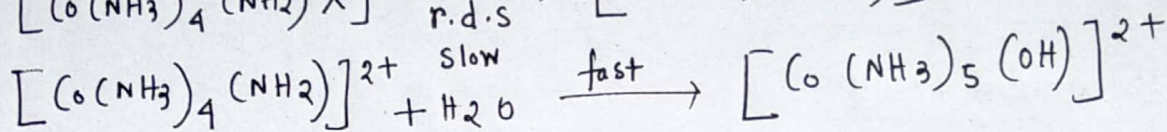
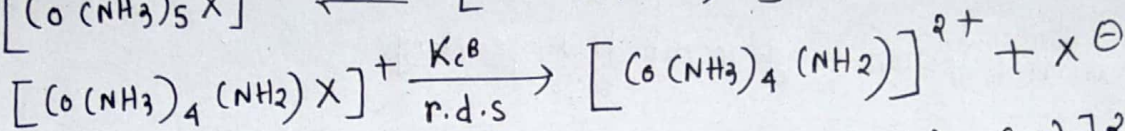
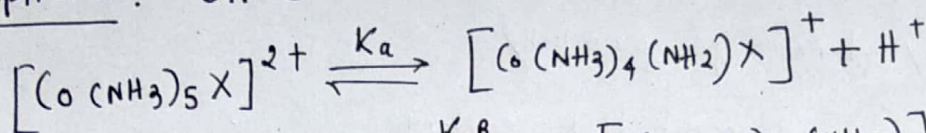


option 1 : Bimolecular reaction ( $SN^2$ )  $\rightarrow$  interchange process (I) (22)



$$\text{Rate} = K_2 [Co(NH_3)_5 X]^{2+} [OH^-]$$

✓ option 2 :  $SN^1CB$  - mechanism  $\rightarrow$  (there are evidences in favour of this mechanism)



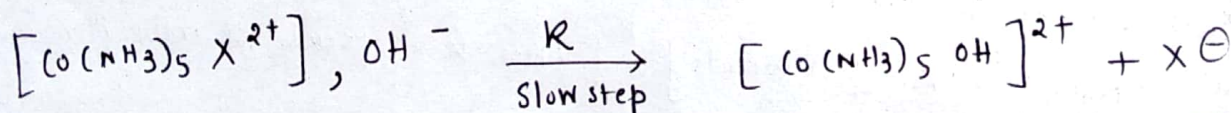
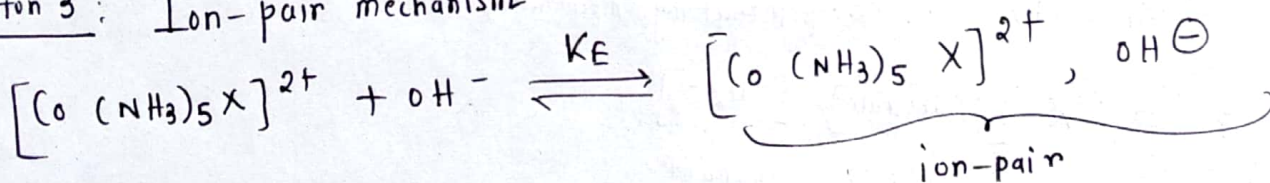
$$\text{Rate} = K_{cb} [Co(NH_3)_4(NH_2)X]^+$$

$$K_a = \frac{[Co(NH_3)_4(NH_2)X]^+ [H^+]}{[Co(NH_3)_5 X]^{2+}}$$

$$\text{Rate} = \frac{K_{cb} K_a [Co(NH_3)_5 X]^{2+}}{[H^+]} = \frac{K_{cb} K_a [Co(NH_3)_5 X]^{2+} [OH^-]}{K_w}$$

$$= K_2 [Co(NH_3)_5 X]^{2+} [OH^-]$$

Option 3 : Ion-pair mechanism



$$\text{Rate} = K [\text{ion-pair}] \left[ \text{Now, } K_E = \frac{[\text{ion-pair}]}{[\text{substrate}] [OH^-]} \right]$$

$$\therefore \text{Rate} = K K_E [\text{substrate}] [OH^-]$$

$$= K_2 [\text{substrate}] [OH^-]$$



# Determinant factors of octahedral mechanism

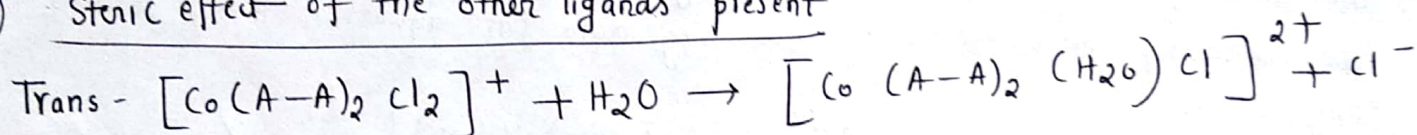
(23)

## (1) The effect of net charge on the complex ion

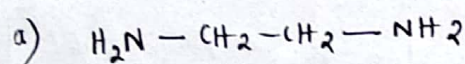
It is observed that, the divalent monochloro complex  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  reacts about 100 times ~~faster~~<sup>slower</sup> (towards acid-catalysed hydrolysis reaction) than univalent dichloro complex  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ .

The effect of this variation of a +ve charge on the complex ion clearly indicates that, the aquation of these complexes takes place via dissociative mechanism. Separation of a -vely charged ion (viz.  $\text{Cl}^-$ ) from positively charged complex ion is more difficult. The greater the amount of +ve charge on the complex, the greater is the difficulty. Hence, the observation. [Hence, option 1 is the correct pathway for acid catalysed hydrolysis reaction, not the solvent path via I-mechanism.]

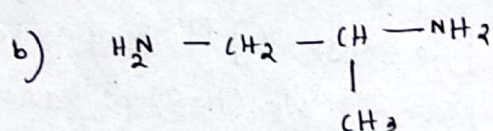
## (2) Steric effect of the other ligands present



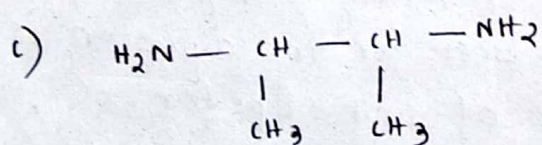
Nature of (A-A) (different diamines)      Rate constant ( $\text{pH} \approx 1$ ,  $25^\circ\text{C}$ )



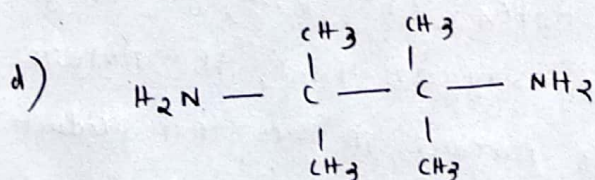
$$3.2 \times 10^{-5} \text{ sec}^{-1}$$



$$6.2 \times 10^{-5} \text{ sec}^{-1}$$



$$15 \times 10^{-5} \text{ sec}^{-1}$$



instantaneous (very very fast)

With increasing bulk of the bidentate chelator present in the substrate the reaction rate increases at a steady rate. It supports dissociative mechanism as well.



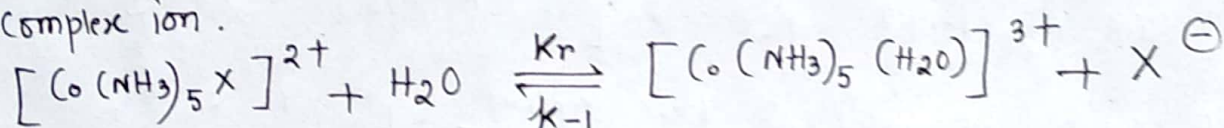
### ③ Linear free energy relationship (Leaving group effects) (L.F.E.R.)

(24)

Many kinetic effects can be related to thermodynamic effects by a linear free energy relationship. Such effects are seen, when, for example, the bond strength of a metal-ligand bond (that is a thermodynamic function) plays a major role in determining a dissociation rate of that ligand (A kinetic function). When it is true, a plot of logarithm of the rate constant (kinetic) for different leaving groups versus the logarithm of the equilibrium const. (thermodynamic) for the same ligands in similar compounds is linear. Or, in other words, in a closely related series of reactions it might be expected that, free energies of activation  $\Delta G^\ddagger$  and free energy of reaction  $\Delta G$  would parallel each other. Such linear free energy relationship might be used in assignment of mechanism by determining the extent of bond formation or breakage in the T.S.

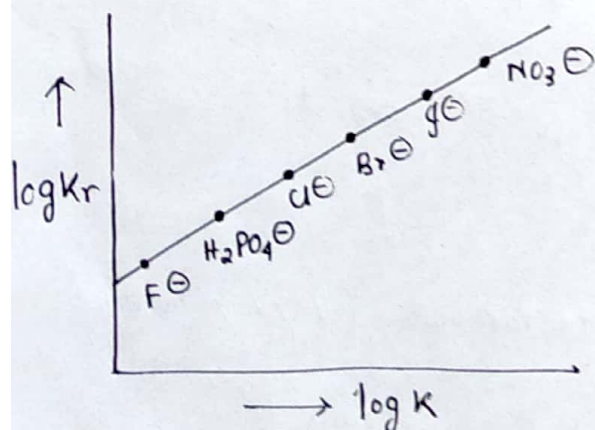
The linearity can be expressed as:  $\log K_r = A \log K + B$

The relationship can be tested by examining data for aquation of a series of complex ion.



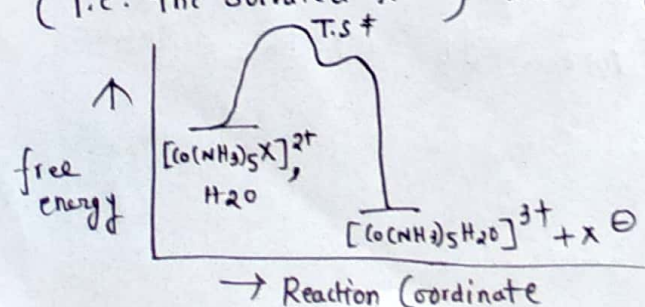
$$\text{eqm. const } K = \frac{K_r}{K_{-1}}$$

$$\therefore \log K_r = A \log K + B \quad [\text{where, } B = \log K_{-1}, A = 1.00]$$



The aquation of  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  leading to the formation of  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  and  $\text{X}^-$ , the plot of  $\log K_r$  vs.  $\log K$ , where  $K_r$  is the eqm. const. for the aquation is a straight line of unit slope for  $\text{X}^-$ ,  $\text{X}^- = \text{F}^-, \text{H}_2\text{PO}_4^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-$ .

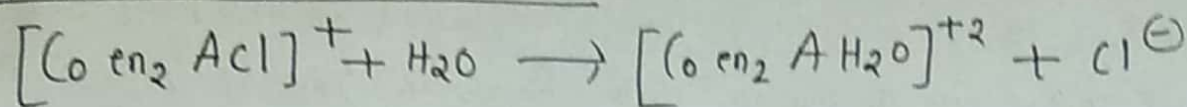
Thus L.F.E.R suggests that, the nature of  $\text{X}^-$  in the transition state resembles its nature in the final product (i.e. the solvated  $\text{X}^-$ ) indicating a dissociative mechanism in which  $\text{Co}-\text{X}$  bond rupture is virtually complete in the transition state.





# The influence of $\pi$ -bonding

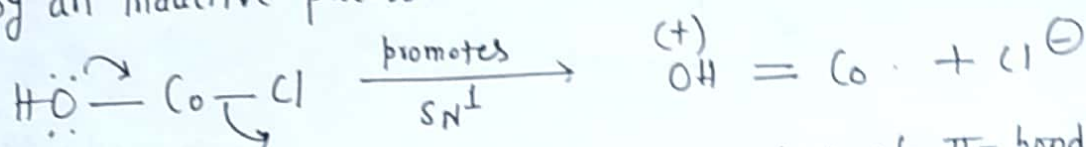
(25)



Isomer	ligand	$k \times 10^5 \text{ sec}^{-1}$
cis	$\text{OH}^-$	1200
cis	$\text{Cl}^-$	24
cis	$\text{NCS}^-$	1.1
cis	$\text{NO}_2^-$	11
trans	$\text{OH}^-$	160
trans	$\text{Cl}^-$	3.5
trans	$\text{NCS}^-$	0.005
trans	$\text{NO}_2^-$	98

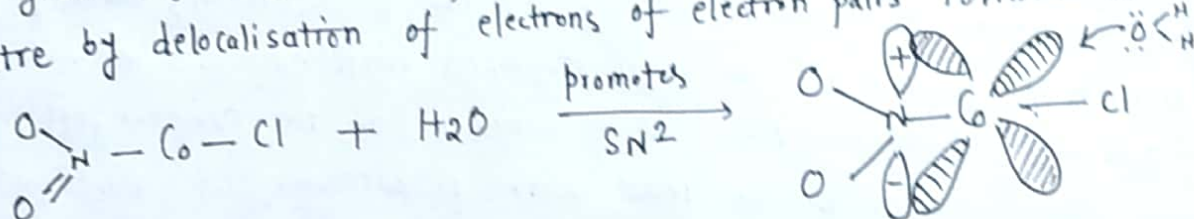
The substituents used in the investigations are of two types.

- a) Ligands possessing lone pairs of electrons which can release electrons by an inductive process.



delocalisation of  $e^-$  pairs results in some extent of  $\pi$ -bonding.

- b) Ligands (eg.  $\text{NO}_2^-$  and  $\text{CN}^-$ ) which can withdraw electrons from the metal centre by delocalisation of electrons of electron pairs towards the ligand.

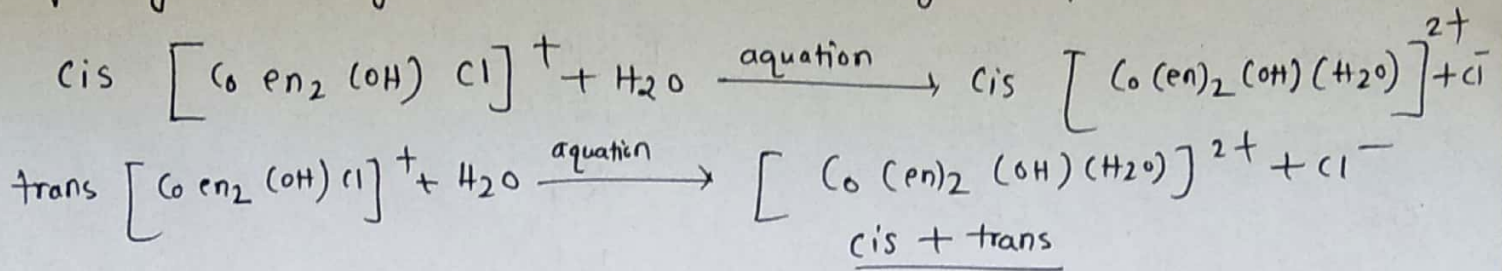


For type 'a' electron displacement occurs from the ligand to the metal making it easier to break the  $\text{Co}-\text{Cl}$  bond. Also, such  $\pi$ -bonding effectively stabilises the 5-coordinated intermediate. A dissociative pathway is thus supported by both the effects.

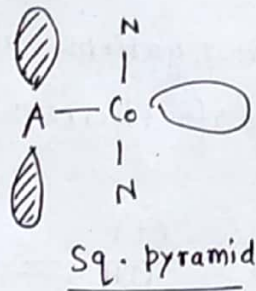
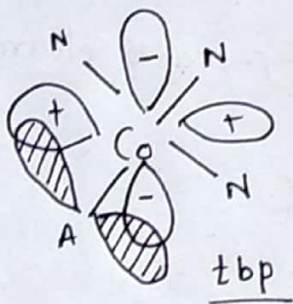
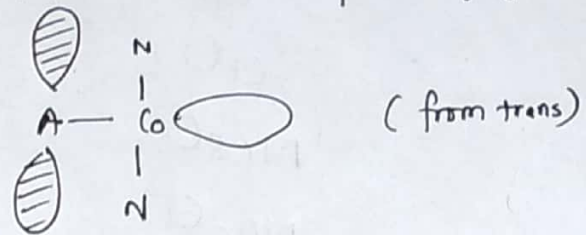
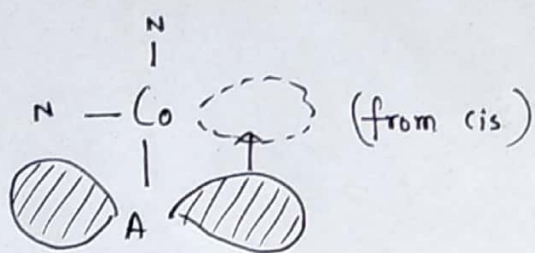
For type 'b' ligands,  $\pi$ -bonding in the direction  $\text{M} \rightarrow \text{L}$  results in strengthening of  $\text{Co}-\text{Cl}$  bond, but at the same time invites nucleophilic attack on the metal centre by an associative mechanism.



Thus the rate of hydrolysis of a series of cis and trans  $Co(en)_2ACl^+$  (eg. given earlier) can be explained on the basis of a gradual change in mechanism with changes in type of 'A' ligand.



For a ligand like  $OH^-$ ,  $Cl^-$ ,  $NCS^-$ , it is seen from the table that cis isomers react more rapidly than the trans (cis-effect). Also, the cis-isomers, unlike trans, react with retention of configuration.



A likely explanation, in terms of  $\pi$ -bonding has been approached. The expulsion of  $Cl^-$  ion and hence the dissociation of cis  $[Co(en)_2ACl]^+$  via a 5-coordinated activated complex will take place readily as a p-orbital on the non-labile ligand A, can form  $\pi$ -bond with ease to a vacant  $d^3sp^3$  orbital of  $Co(III)$ . Also, in this scheme, as no rearrangement is necessary, cis-isomers should react with retention of configuration. In case of trans- $[Co(en)_2ACl]^+$ , the 'p' orbital on  $OH^-$  ion cannot overlap a vacant  $d^2sp^3$  orbital without substantial rearrangement. The rate of activation of such trans isomer is thus predicted to be lower than its cis-analogue.



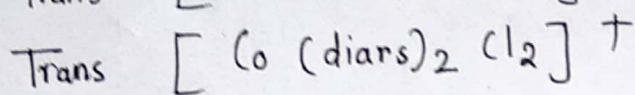
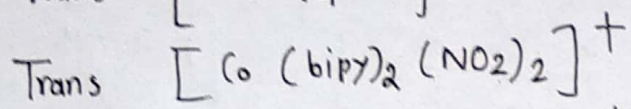
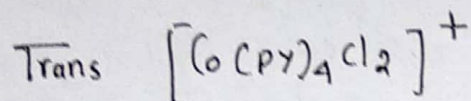
## Mechanism of base hydrolysis of Co(III) complex

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Three probable pathways : i)  $S_N2$  ii)  $S_N1CB$  (iii) ion-pair

### evidence in favour of $S_N1CB$ mechanism

1. Effect of absence of acidic proton in the complex



It is predicted that complexes without acidic protons will not react rapidly with hydroxide ion. This is true for complexes  $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$  and  $[\text{Co}(\text{CN})_5\text{I}]^{3-}$  which hydrolyse at a rate independent of pH over the alkaline range. In these cases of negatively charged ions, the failure to form activated complex with hydroxide ion may be due to electrostatic repulsion. Compounds without acidic proton react at a rate independent of pH and the fact supports  $S_N1CB$  mechanism.

2. The effect of net charge of the complex ion on the rate :

<u>Complex ion</u>	<u>Rate constant</u>
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	$8.5 \times 10^{-10} \text{ lit mol}^{-1}$
trans $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$	$1.8 \times 10^3 \text{ lit mol}^{-1}$

Doubly charged Co(III) complexes undergo base hydrolysis 200 to 300 times more slowly than the singly charged complex. This fact is compatible with  $S_N1CB$  mechanism.

### Comparison between rates of acid hydrolysis and base hydrolysis

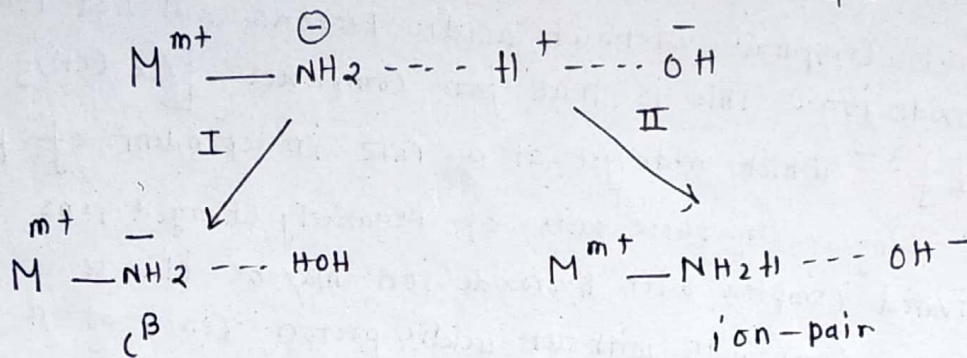
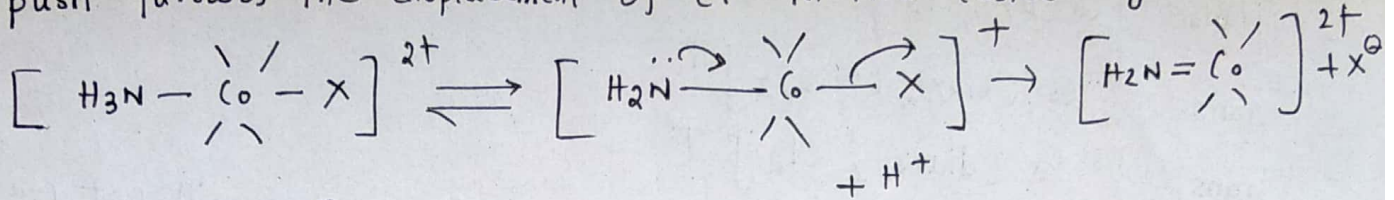
The rate constants for acid and base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  are :

$$\left. \begin{array}{l} K_{\text{H}_2\text{O}} = 6.7 \times 10^{-6} \text{ sec}^{-1} \\ K_{\text{OH}^-} = 8.5 \times 10^{-1} \text{ sec}^{-1} \end{array} \right\} \text{ at } 25^\circ\text{C}$$



Thus, the rate of base hydrolysis is manifold faster than the acid-hydrolysis. According to the supporter of  $S_N^2$ -process, this is due to difference in nucleophilic character of  $OH^-$  and  $H_2O$ . But this fact only donot account for such a great difference.

According to  $S_N^1CB$  process, the amine complex is converted in an acid-base equilibrium step as an amino complex and the lonepair on amide is added to the Cobalt atom, consequently an electrostatic push favours the displacement of  $Cl^-$  in the easier way.



It has been suggested that the conjugate base and ion-pair are the two limiting states of the following system.



(Depending upon, whether the proton is primarily under the control of  $OH^-$  ion or  $NH_2^-$  ion respectively). Ion pair or conjugate base formation depends on the nature of the substrate complex. If the amine complex contains a strong electron withdrawing group bounded to the metal ion, the acidity of the amine proton is then sufficiently increased to allow a complete transfer of the proton to the  $OH^-$  producing the  $CB$ , otherwise, the ion-pair formation is favoured.